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Development of Contaminant Generation Systems for Certification of Portable Air Sampling Instruments

B. C. Cadoff, B. Greifer, P. A. Pella, and J. K. Taylor

National Bureau of Standards
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Washington, D. C. 20234

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Annual Report

Prepared for
National Institute for Occupational Safety and Health
Testing and Certification Laboratory
Morgantown, West Virginia

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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Development of Contaminant Generation Systems for Certification of Portable Air Sampling Instruments

ABSTRACT

The development of gas generation systems is described. Stable mixtures of contaminant gases with air are stored in compressed gas cylinders at concentrations about five times the Threshold Limit Values (TLV). The cylinders are analyzed by charcoal tube gravimetry in which the weight increase of tared charcoal tubes is used to determine the organic component of the gas mixture. For use, the compressed gases are dynamically diluted with air to the needed concentrations in a gas-flow system.

Data are presented to demonstrate (1) linearity of the gas dilution system as measured by gas chromatographic determinations of vapor concentrations; (2) precision of charcoal tube gravimetric measurements; and (3) stability of compressed gas mixtures of air with chloroform, toluene, methylene chloride, ethylene dichloride, 1,1,1-trichloroethane, and styrene at concentrations of 1210, 650, 4850, 980, 1940, and 475 ppm respectively.

It is concluded that the methods of preparation and verification of these compressed vapor-air mixtures have general applicability. A wide variety of stable single-component vapor-air mixtures may be prepared and analyzed to one percent accuracy rapidly and routinely.

1. INTRODUCTION

This report summarizes work concerned with the development of systems to generate test atmospheres useful for verifying the performance of gas analysis instrumentation. It is part of an ongoing program at the National Bureau of Standards under sponsorship of the National Institute for Occupational Safety and Health (NIOSH) to assist the latter agency in its measurement methodology certification program. A previous report - NBSIR 73-292, Gas Generation Systems for the Evaluation of Gas Detecting Devices, October 1973 - deals with the general philosophy and describes gas generation systems for a number of mixtures based on several generating principles. The present report is an extension of this work and is devoted to gas mixtures containing organic substances, and especially organic solvents.

2. TECHNICAL APPROACH

Some organic substances commonly found as contaminants of industrial work atmospheres are listed in table 1. The present investigation is concerned with the first six of these. Test atmospheres of these substances should be readily generated by the dilution of concentrated bulk mixtures with air in dynamic blending systems such as described in the earlier report, if the bulk mixtures are of sufficient stability. Even in the case of limited long-term stability, this approach is feasible, provided the bulk mixture can be analyzed at the time of use.

The work involved the following tasks: preparation of bulk mixtures; investigation of stability of bulk mixtures; development of analytical methodology; evaluation of the dilution system.

3. PROJECT PLAN

3.1 Bulk Mixtures

Gas mixtures consisting of a single component in air or other diluent gas are readily prepared in compressed gas cylinders of the type used for industrial gases, to give long-lasting supplies of the known mixtures. Liquids may be introduced into the gas cylinders by vapor distillation or by direct injection in an amount calculated to give the desired concentration of the organic ingredient after the cylinder is pressurized with diluent gas. Vapor pressure considerations are important, for too high an organic vapor concentration can cause condensation within the cylinder (with resultant change of mixture composition) at lowest operating temperatures.

For maximum stability the mixture concentration should be as high as possible consistent with vapor pressure limitations because low-concentration mixtures in the ppm range are especially susceptible to loss of material through vapor sorption on the cylinder walls. While high-concentration mixtures are subject to the same sorption losses, there is opportunity for eventual stability to be attained through surface saturation; also, the higher concentration mixtures would be subject to smaller relative errors from this cause.

The following working standards were prepared with air as the diluent gas: chloroform (1210 ppm), toluene (650 ppm), methylene chloride (4850 ppm), ethylene dichloride (980 ppm), 1,1,1-trichloroethane (1940 ppm), and styrene (70 and 475 ppm). Details of preparation are given in Section 4.

Table 1. Organic contaminants

Contaminant	TLV ¹ (ppm)	Concentration Range	
		(ppm)	
1. Chloroform	50	12.5	to 125
2. Toluene	200	50	to 500
3. Methylene Chloride	500	250	to 2500
4. Ethylene Dichloride	50	25	to 250
5. 1,1,1-Trichloroethane	350	175	to 1750
6. Styrene	100	50	to 500
7. Carbon Disulfide	50	10	to 100
8. Vinyl Chloride	0 ²	100	to 1000
9. Acetone	1000	500	to 5000
10. Methyl Ethyl Ketone	200	100	to 1000
11. Chlorobenzene		37.5	to 375
12. Aniline	5	2.5	to 25
13. Phenol	5	2.5	to 25

¹These values from Federal Register 36 (157), Aug. 13, 1971.

²Formerly 500 ppm, then 50 ppm, now reported to be zero.

Table 2. Vapor pressures of solvents of interest¹

Condensation Temperature (°C) at Indicated Pressures (mm Hg)

Solvent	1mm	10mm	40mm	100mm	400mm	760mm	1520mm
1. Chloroform	-58.0	-29.7	-7.1	10.4	42.7	61.3	83.9
2. Toluene	-26.7	6.4	31.8	51.9	89.5	110.6	136.5
3. Methylene chloride	-70.0	-43.3	-22.3	- 6.3	24.1	40.7	
4. Ethylene dichloride	-44.5	-13.6	10.0	29.4	64.0	82.4	108.1
5. 1,1,1-Trichloroethane	-52.0	-21.9	1.6	20.0	54.6	74.1	
6. Styrene	-7.0	30.8	59.8	82.0	122.5	145.2	
7. Carbon disulfide	-73.8	-44.7	-22.5	- 5.1	28.0	46.5	69.1
8. Vinyl chloride	-105.6	-83.7	-66.8	-53.2	-28.0	-13.8	
9. Acetone	-59.4	-31.1	- 9.4	7.7	39.5	56.5	78.6
10. Methyl ethyl ketone	-48.3	-17.7	6.0	25.0	60.0	79.6	
11. Chlorobenzene	-13.0	22.2	49.7	70.7	110.0	132.2	160.2
12. Aniline	34.8	69.4	96.7	119.9	161.9	184.4	212.8
13. Phenol	40.1	73.8	100.1	121.4	160.9	181.9	208.0

¹Handbook of Chemistry and Physics, Chemical Rubber Co., 49th ed. (1968-1969), pp D-120 to D-136.

3.2 Gas Analysis

The method of preparation can serve as a means for determining the initial composition of the resultant gas mixtures since known quantities of solvent vapor are diluted with known volumes of air. However, this calculated composition is good to only a first approximation because (1) there is no assurance that all of the vapor or liquid introduced into the compressed gas tank is available since loss can occur due to sorption on the interior tank surface, and (2) there are uncertainties regarding the equation-of-state for the particular system. Furthermore, it is necessary to be able to analyze the bulk mixtures at any later time to verify their concentrations.

An unambiguous and absolute procedure involving sorption on activated charcoal was developed. The procedure, referred to as charcoal tube gravimetry, should prove useful for a wide range of organic solvents, giving results that are accurate to about one percent. A charcoal tube of the type used for sampling industrial atmospheres is used to sample the gas mixture for a precisely determined time and at a constant flow rate. The weight of the sorbed material and the total volume sampled are used to calculate the gas concentration. Details are given in Section 4.2.

3.3 Stability

The stability of the prepared gas mixtures was measured by charcoal tube gravimetry over a period of 2 to 6 months between October 1973 and July 1974. Four measurements made in 1973 were not included in the final data averages because refinements in the measurement techniques (i.e. precise calibration of the flowmeter, measurement of actual gas flow through each charcoal tube, elimination of static electricity effects during weighings, etc.) made these first analyses less dependable than desired, even though they differed by only one to five percent from the 1974 analyses.

3.4 Performance Evaluation

The analysis of the working standards and the output mixtures of a gas dilution system using a gas chromatograph gave straight line plots passing very near the origin, thus demonstrating the reliability of the dynamic dilution procedure. Charcoal tube gravimetry was also used to measure the concentrations of some of the mixtures produced by gas dilution.

The relative standard deviation of all the charcoal tube measurements and the gas chromatographic analyses did not exceed two percent, and in most cases was one percent.

3.5 Delivery of Working Standards

Compressed gas cylinders delivered to NIOSH at the completion of this program included chloroform (1210 ppm), toluene (650 ppm), methylene chloride (4850 ppm), ethylene chloride (980 ppm), 1,1,1-trichloroethane (1940 ppm) and three cylinders of styrene (475 ppm average). The 70 ppm styrene tank which had been prepared especially for analytical experimentation and stability studies was not delivered.

4. EXPERIMENTAL DETAILS

4.1 Preparation of Compressed Gas Mixtures

Volatile solvents are distilled into evacuated compressed gas cylinders to the desired partial pressure as measured by a mercury manometer. The partial pressure must not exceed the saturation vapor pressure of the solvent at the lowest temperature of use, for the resulting condensation will change the mixture composition. Solvents of low volatility are injected directly into the evacuated cylinders through a rubber septum, using a weighed hypodermic needle. The cylinders are pressurized with air to a suitable total pressure to dilute the inserted solvent vapors to the desired trace concentrations.

Compressed gas cylinders of chloroform, toluene, methylene chloride, ethylene dichloride, and 1,1,1-trichloroethane were prepared by distilling the solvent vapors into evacuated tanks to the appropriate vapor pressures, then filling the tanks with breathing air to yield mixtures containing the organic solvents at the desired concentrations. Styrene was injected directly into cylinders through a rubber septum because the low vapor pressure would have required inordinately long distillation time with resultant risk of room air contamination through chance leaks. The weight of styrene injected was determined by weighing the hypodermic syringe before and after injection.

The gas cylinders were pressurized with air to give the desired vapor concentrations according to the following expression derived from the gas laws:

$$C_V = \frac{P_V (14.7 \times 10^6)}{P_T 760} \quad (1)$$

where C_V = concentration of vapor in tank (ppm)
 P_V = partial pressure of vapor in tank (mm Hg)¹
 P_T = total tank pressure (psia)²
14.7/760 = psia/mm conversion
 10^6 = factor for parts per million conversion

This is an approximate calculation because it assumes that the ideal gas laws hold at both low and high pressures. However, this equation is sufficient for the purpose.

4.1.1 Vapor Distillation

Select a new compressed gas cylinder (preferably) or one that has been used only for air or water-pumped nitrogen. The tank may be filled with solvent vapor using pressure-vacuum instrumentation similar to that diagrammed in figure 1.

1. With a full (2000 psig) cylinder of breathing air on line 1, and the empty or new cylinder on line 4 but with all valves closed, start the vacuum pump, then open valves 5, 7, 8, 9, 10 and 4 in that order, to evacuate the system down to minimum attainable pressure as read on the absolute pressure gauges.

2. Check for vacuum leaks by closing valve V-5 and noting any pressure rise in the system. If the pressure does not increase after 30 min the system is considered to be vacuum tight. Close all valves.

3. Check for pressure leaks by opening valve V-1, close it immediately, then open V-7 slowly to admit less than 1000 psi then close it, open V-8 slowly to admit less than 500 psi then close it, then V-9 to less than 100 psi,

¹ 1 mm Hg = $\frac{101325}{760}$ pascals = 133.32 Pa

² 1 psia = $\frac{101325}{14.7}$ pascals = 6892.9 Pa

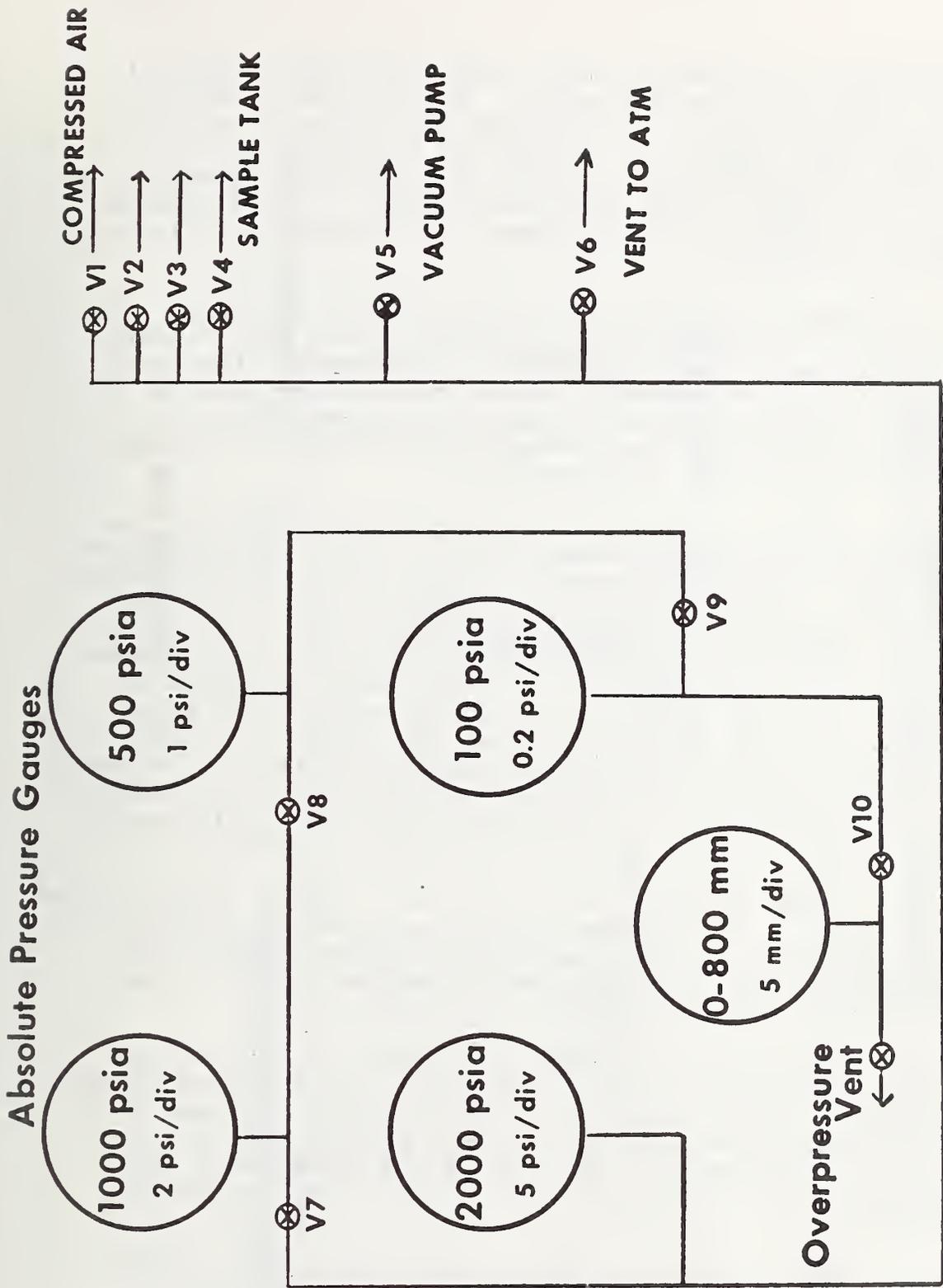


Fig. 1 INSTRUMENTATION FOR FILLING COMPRESSED GAS CYLINDERS

and V-10 to less than 800 mm, close all valves rapidly to avoid overpressuring the gauges. Now all the valves are closed and all the pressure gauges are reading near their maximum scale readings. Observe the system for 30 min and note that there is no pressure drop. The system is ready to be used. Open valve V-6, then V-7, 8, 9, and 10 in order to bleed the system down to atmospheric pressure. Close all valves.

4. Flush the sample tank three times by applying vacuum and pressurized air alternately using only valves V-1, 4, 5, and 6 for the purpose. This removes traces of moisture found occasionally in new tanks after factory pressure testing. Leave the tank fully evacuated, disconnect it from line 4 and connect it to the solvent vapor filling system shown in figure 2.

5. Connect the solvent filling system (figure 2) to the pressure-vacuum instrumentation through line 4 (figure 1) and open all valves, except V-13, 1, 2, 3, 6 to evacuate the system. Check for leaks under vacuum as outlined in step 2, keeping valves 4 and 12 open and valves 11 and 13 closed. The mercury manometer as read with a cathetometer is a suitable leak detector; it should show no pressure increase from the minimum attainable pressure even after 30-60 min. It is safe now to open the sample cylinder to the system, noting that there should be no pressure increase; if there is, check for leaks between the system and sample tank. Re-evacuate the system and assure that there are no vacuum leaks. Record the mercury manometer reading.

6. Close valve V-4 and open V-11 to admit solvent vapor to the system. The manometer pressure rises as solvent boils and distills into the sample cylinder. Admit the vapor slowly, chilling or warming the glass bulb of the solvent reservoir as required.

7. When the desired partial pressure of vapor has been attained close V-11 and allow the system to equilibrate for 30 min. Then, close the sample cylinder and open vent V-13 cautiously to avoid forcing the mercury out of the manometer, and open V-11 to relieve the vacuum over the solvent. Now, close valves V-11, 12, 13, and the sample cylinder.

8. The cylinder is ready to be pressurized. Tape a thermometer to the cylinder and cover the bulb with several layers of insulating material so that the tank temperature not the room temperature is read. With the air tank still on line 1 and the sample filling system still on line 4, all valves closed, open valve V-1 slightly and

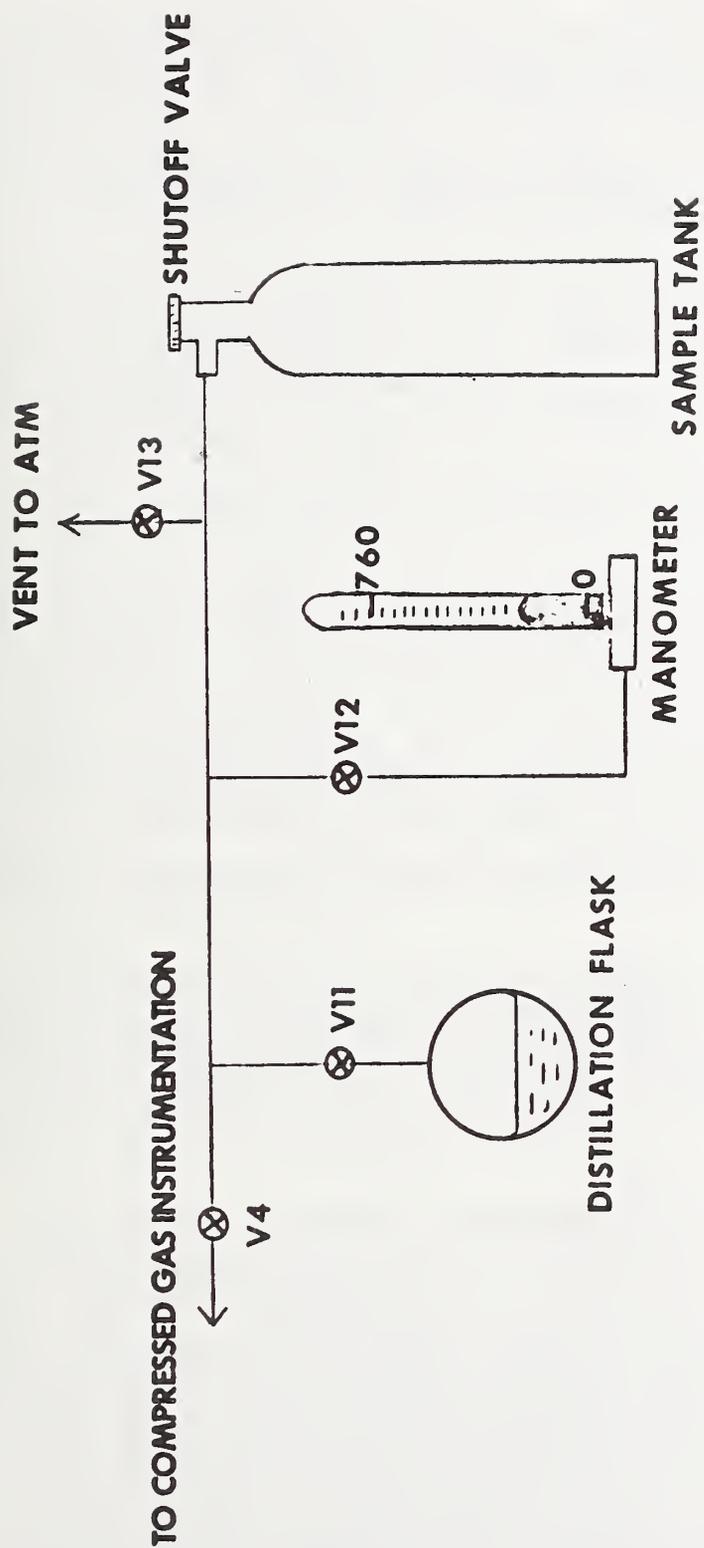


Fig.2 SOLVENT VAPOR FILLING SYSTEM

allow the pressure to build up slowly on the 2000 psia gauge. Open V-4 and V-13 to flush out the lines; then, close V-13 and open the sample cylinder.

9. Keep a close control over V-4 to prevent the compressed air from surging too rapidly into the evacuated sample tank. When the pressure is nearly at the desired value, say 1000 psia, close the sample tank, then valves V-1 and V-4 and allow the tank which has been heated by compression of its contents to cool for several hours or overnight if possible.

10. After temperature equilibration, the pressure is adjusted to the final value. The valve adjustments must be made in such a way that the gauge pressure always exceeds the sample tank pressure so that the flow is always from the air supply to the sample tank and never in the reverse direction (loss of organic vapor might otherwise occur). This is accomplished by assuring that the sample tank valve is opened last and closed first in any pressure adjustment.

11. Set the air supply to the desired tank pressure with valve V-1, using as many gauges as necessary to read the final pressure most accurately. With V-1 closed and V-4 open, crack the sample tank valve until the gauge readings stop falling, and close it immediately. Repressurize with V-1 and repeat the process in small pressure steps until the sample tank pressure is at the desired value. Record the pressure and temperature of the tank.

12. Vent the air supply system to atmospheric pressure with either V-6 or V-13.

13. Mount the sample tank in an inclined position (use a cylinder cart) and heat the bottom gently with an infrared light for at least three hours to mix the contents. Overnight is a convenient mixing period. The tank is ready for use after suitable labeling of the contents.

4.1.2 Liquid Injection

Styrene and other solvents of low volatility are handled somewhat differently because their low volatility would require an inordinately long distillation time for the partial pressures to build up to the desired values. The effects of minute system leaks, undetectable during 30-60 min of leak testing would be magnified during a 3-4 hr vapor distillation, and any pressure increase due to air would be read as vapor partial pressure. Warming the distillation flask to accelerate distillation is not an acceptable procedure for styrene because of the danger of polymerization. It is best to inject the liquid directly into the sample tank in these cases.

A rubber septum of the type used for gas chromatographic injection is mounted in one arm of a tee compression tube fitting which is threaded onto a CGA fitting that fits directly into the sample tank inlet. The third arm of the tee is attached to valve V-4 of the pressure-vacuum instrumentation (figure 1) and the following procedure is employed.

1. The previously evacuated and air-flushed tank is leak tested for 15-30 min under pressure (40 psia maximum) and for 30-60 min under vacuum to assure that the rubber septum and associated connections are tight.

2. Fill a hypodermic syringe with a suitable volume of styrene and seal the syringe by pushing the tip into a spare rubber septum to cut down evaporation losses. Weigh the filled syringe.

3. Plunge the syringe deeply into the rubber septum fitting past the tee side-arm into the throat of the opened evacuated sample tank, and inject the contents rapidly into the fitting. The vacuum inside the fitting will assist the operation. Remove the syringe, cap with the same rubber septum, and weigh to determine the amount of styrene injected.

4. Flush the styrene into the tank by piercing the septum with a hypodermic needle, leaving it to bleed atmospheric air into the sample tank for 30-60 min. The fitting may be warmed with an infrared heat lamp during this operation. When the sample tank is almost at atmospheric pressure but still under slight vacuum, close the tank and remove the special fitting.

5. Connect the tank to valve V-4 of the pressure-vacuum instrumentation board and pressurize to the desired value with breathing quality air as described in steps 8-13 for vapor distillation. The tank contents are mixed for several hours or overnight using a heat lamp directed at the base to generate convection currents.

4.1.3 Estimation of Target Concentrations

4.1.3.1 Vapor Distillation

The compressed gas mixtures were prepared at the highest concentrations possible short of causing condensation inside the sample tanks. The limiting concentration is that at which the partial pressure of the solvent vapor reaches the saturation pressure at the temperature of use, which may be in the range 20-25 °C. (However, if the cylinder is outdoors on a cold day, condensation may occur with resultant change of gas composition; and it is not known how long it may take

to re-vaporize and mix the contents when the cylinder is returned to room temperature.) Consequently, the vapor pressures of the inserted solvents were kept below the 20 °C levels in most cases to permit the tanks to be unharmed by temperature excursions somewhat below this value.

Table 2 shows the condensation temperatures of 13 solvents for seven pressures between 1 mm Hg and 2 atm. Figure 3 plots these data and shows the maximum partial pressures that can be tolerated in the gas cylinders at any given temperature. To provide a margin of safety, the cylinders were filled to somewhat lower partial pressures so that they might be used at temperatures of 15-18 °C if necessary.

The required partial pressure of the solvent vapor may be estimated from the pressure-volume relationships obtained by rearranging Eq. (1); or, knowing the partial pressure to which solvent vapor was permitted to distil, the equation permits calculation of the pressure to which the tank should be filled with breathing air for chosen values of mixture concentration. Table 3 summarizes the calculated and measured concentrations for the five volatile solvents.

Table 3. Concentrations of volatile solvent mixtures

<u>Ingredient</u>	<u>Partial pressure (mm)</u>	<u>Cylinder pressure (psia)</u>	<u>Calculated concentration (ppm)</u>	<u>Average measured concentration (ppm)</u>
Chloroform	65.4	1000	1265	1210
Toluene	27.0	875	597	650
Methylene Chloride	259.0	1000	5000	4850
Ethylene Dichloride	44.3	837	1024	980
Trichloroethane	79.75	786	1963	1940

4.1.3.2 Liquid Injection

Since the saturation pressure of styrene is about 5.5 mm at 20 °C it is desirable that the partial pressure P_v not exceed about 4 mm to avoid the possibility of condensation, especially since it is not known how difficult it may be to revolatilize the styrene inside the gas tank without heating and attendant risk of polymerization.

The volume of liquid styrene needed to yield a partial pressure of 4 mm in a compressed gas tank having an average volume of 42 liters is given approximately by the expression:

$$V_L = P_v V_T \left(\frac{M}{d} \right) \left(\frac{1}{24.5 \times 760} \right) \quad (2)$$

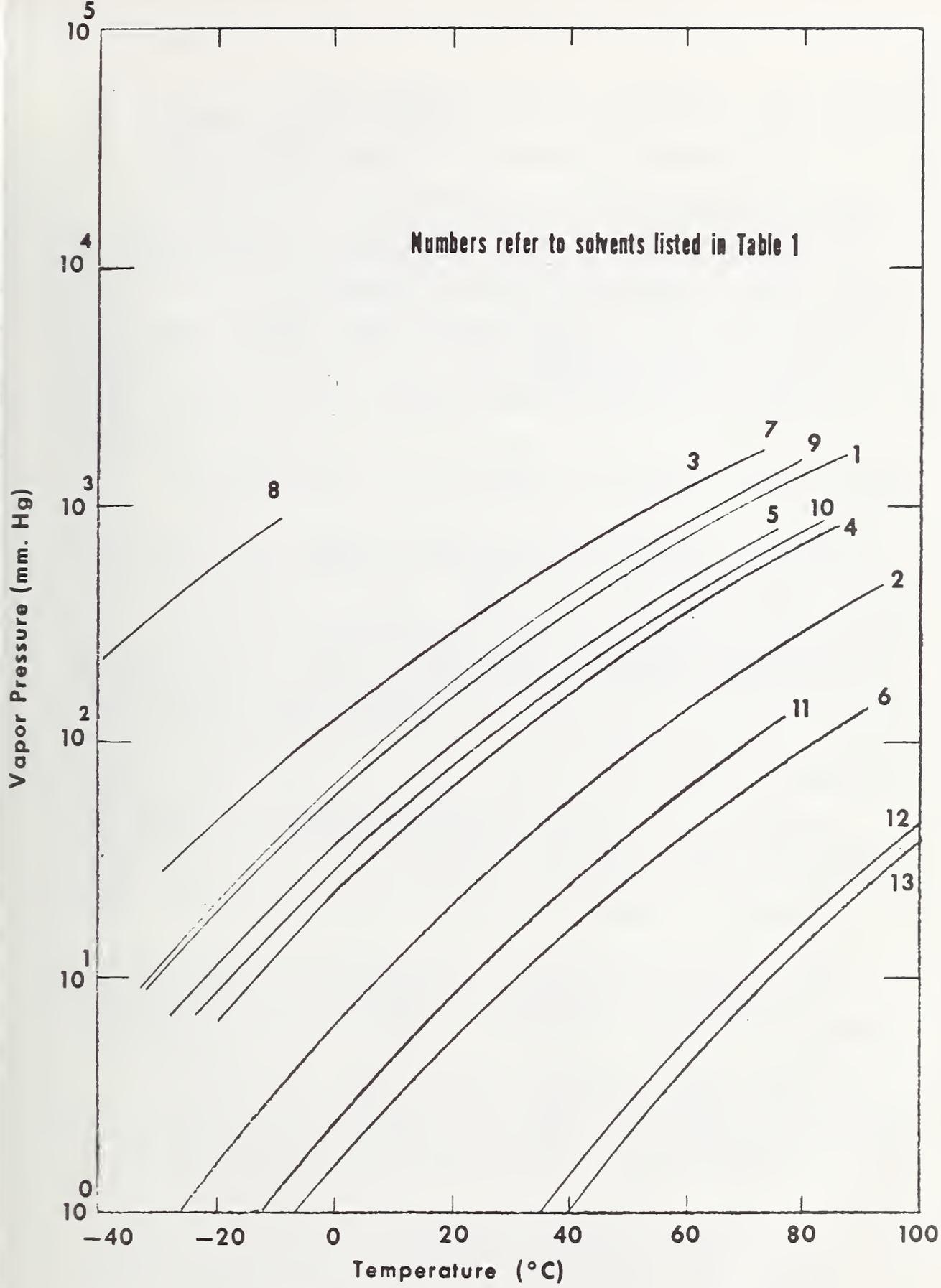


Fig. 3 VAPOR PRESSURE OF SOLVENTS

where: V_L = volume of liquid styrene (ml)
 P_v = partial pressure of styrene vapor = 4 mm
 V_T = total volume = 42 liters
 M = molecular weight of styrene = 104.14 g/mole
 d = density of styrene = 0.909 g/ml
24.5 = volume of one mole of ideal gas at 25 °C
and one atm.
760 = atmospheric pressure (mm)

The volume needed is 1.0 ml, or 0.9 g styrene and this information is useful for choosing the proper size of syringe.

Equation (1) may now be used to calculate the total pressure to which the styrene tanks should be filled to reach a concentration of 500 ppm. This is approximately 150 psi for the assumed 4 mm vapor pressure, which is not enough styrene mixture for the required exploratory gas chromatographic experiments and charcoal tube gravimetric analyses. Consequently, an additional mixture pressurized to over 800 psi was prepared for the exploratory experiments. Three gas tanks pressurized to the required 150 psia were prepared also for final analysis and delivery to NIOSH.

Table 4 presents the calculated and measured concentrations for the styrene working standards.

Table 4. Concentrations of styrene gas mixtures

<u>Ingredient</u>	<u>Weight injected (g)</u>	<u>Cylinder pressure (psia)</u>	<u>Calculated concentration (ppm)</u>	<u>Measured concentration (ppm)</u>
Styrene	0.980	843	97	70
Styrene-1	1.025	150	562	475
Styrene-2	1.040	150	571	
Styrene-3	1.034	150	567	

4.2 Charcoal Tube Gravimetry

4.2.1 Summary of Method

Gas mixtures containing organic vapors that are capable of being quantitatively adsorbed by activated charcoal may be analyzed for their organic vapor content by determining the weight gain of the charcoal corresponding to known volumes of gas. The gas mixtures are sampled at precisely measured flow rates through tared charcoal tubes of the type used for air pollution analysis and their weight gain, translated into volumes of gas sampled, gives the organic vapor concentrations in ppm. Figure 4 is a diagram of the charcoal tube gas sampling system.

4.2.2 Experimental

1. Select three (3) charcoal tubes that have been stored in the presence of silica gel. Since the tube ends are not fire polished, avoid tubes that exhibit rough edges from which bits of glass can break off and change the tares.
2. Wipe the tubes with a lintless tissue to remove surface film and dust. Thereafter, the tubes may be handled lightly with bare hands except when gripping them tightly (as for insertion into the plastic end caps) when they should be protected with a tissue.
3. Insert the tubes into holders connected to critical flow orifices (figure 4) and insert the open ends into a gas manifold through which breathing quality air is already flowing from a compressed gas cylinder at a rate about twice the total sampling rate through all the orifices (e.g. 6-8 L/min for three 1-L/min orifices). Open the vacuum sampling cock.
4. After 10-15 min flow turn off the sampling vacuum, remove the tubes, cap them (use tissue) and set them near the balance to equilibrate for temperature and humidity. This may be as long as 1-hr. Disconnect the compressed air from the manifold.
5. Weigh the tubes. It is recommended that the balance be equipped with an ionizing device to minimize the effects of static electrical charges on the glass tubes; this is especially important on days of low humidity, i.e. less than 30 percent R.H.
6. Repeat the conditioning treatments until two successive weighings show that the tubes have attained constant weight within $\pm 50 \mu\text{g}$. Repetitive conditioning

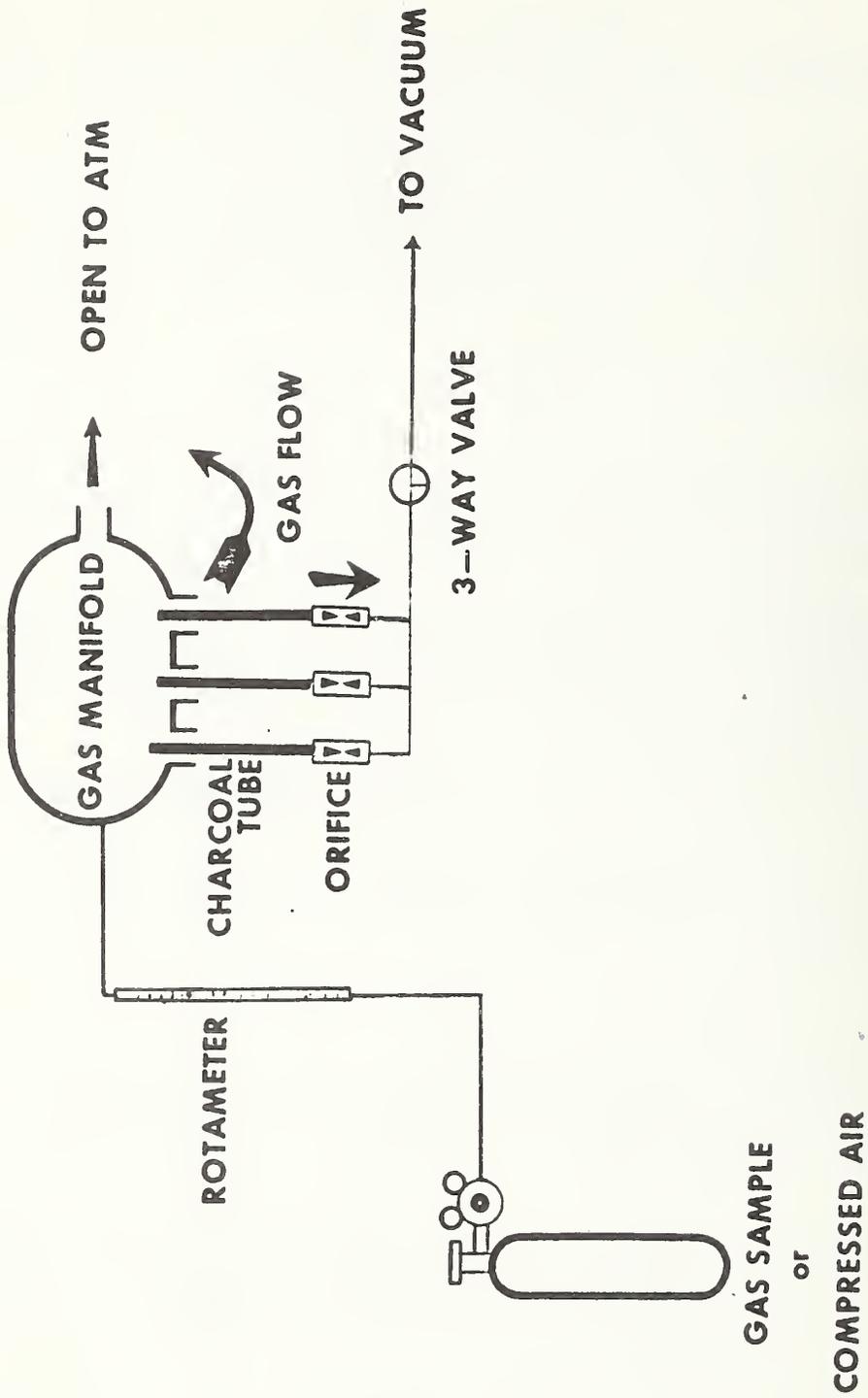


Fig. 4 CHARCOAL TUBE GAS SAMPLING SYSTEM

treatments are recommended for each new lot of charcoal tubes to establish the total air pretreatment required for the tubes to attain constant weight. Thereafter, the tubes may be conditioned once for this total time. The initial repetitive weighings for each lot of tubes may be avoided by conditioning for a long time, say 1-hr, but this is risky because some lots of tubes may require even longer conditioning, and some may require only a short conditioning time.

7. Record the constant weight (average of three readings for each weighing) as the tare. Place the tubes in separate envelopes with identifying numbers corresponding to the three orifices to be used for sampling.

8. Flush the gas manifold with the contaminant gas mixture for 3-5 min at 6-8 L/min. Remove the plastic end caps from the tubes, saving them in numbered envelopes. Pay special attention to the end caps to avoid mixing them. Insert the tubes in their correspondingly numbered orifices while the contaminant gas is flowing.

9. With a stopwatch already running, open the vacuum cock to the sampling orifices when the pointer passes an index, and time for exactly 2, 4, 10, 20 min etc. to collect about 6-15 mg on the charcoal. End the sampling when the pointer passes the index after the desired time by turning the vacuum cock to simultaneously shut off the vacuum and open the orifices to the atmosphere. (It is not sufficient to merely shut off the vacuum because the critical flow orifices would continue to sample for several seconds afterward, until the pressure across them equalizes.) Shut off the contaminant gas flow.

10. Cap the charcoal tubes with their own end caps, permit them to equilibrate near the balance (1-hr used in this laboratory), and weigh them to determine the sample weight. The tubes may be used for a second sample collection if their breakthrough capacity has not been reached.

11. After the gas sampling experiments are concluded, return the charcoal tubes to their critical flow orifices and confirm the sampling flow rates of the orifices plus charcoal tubes with a wet-test meter. Connect the orifices one at a time to the downstream side of the meter, leave the upstream side open to the atmosphere. When the vacuum sampling valve is turned and vacuum is applied, air flows through the meter into a charcoal tube and orifice. Time the flow rates for at least one complete revolution of the meter pointer.

4.2.3 Calculations

The concentration of the organic constituent in a gas mixture is calculated from the weight of adsorbed material, sampling time, and flow rate by a simple relationship derived from the gas laws:

$$C_v = \frac{W}{Mrt} (24,450) \quad (3)$$

where C_v = concentration (ppm)

W = weight increase of charcoal tube (mg)

M = molecular weight of organic vapor (g/mole)

r = flow rate (liters/min) corrected to STP³

t = sampling time (min)

24,450 = volume of one mole of gas (ml) at STP³

³Since the flow rates are measured with a wet-test meter their correction to STP (standard temperature and pressure, 25 °C and 760 mm) are carried out conveniently by application of the wet-test meter equation reproduced here for convenience:

$$r_{STP} = r_m \cdot V_{Mtr} \cdot \frac{298.16}{T_m} \cdot \frac{P_{bar} - P_g}{760} \quad (4)$$

where: r_{STP} = corrected flow rate (liters/min)

r_m = measured flow rate (liters/min)

V_{Mtr} = volume of wet-test meter determined by calibration = 1.024 liter/rev for meter used

T_m = temperature of water in wet-test meter (°K)

P_{bar} = barometric pressure (mm Hg) corrected for scale expansion referred to 0 °C

P_g = back pressure on wet-test meter (mm Hg)

Since the critical flow orifices are downstream of the wet-test meter during the flow calibrations, the vapor pressure of water at the measured temperature does not enter into the equation.

4.3 Gas Chromatographic Analysis of Gas Mixtures

The concentrated gas mixtures which have been analyzed by charcoal tube gravimetry, i.e. the working standards, are diluted to the desired concentrations with the aid of gas mixing systems such as have been described in previous reports.⁴ The diluted gas mixtures may be analyzed rapidly and effectively by gas chromatography to confirm the proper operation of the gas dilution system. This section describes the analytical procedures used, and demonstrates the feasibility of using a gas chromatograph to analyze gas mixtures at all dilutions from the original working standard concentration to the lowest concentrations of interest, about 1/2 TLV.

The response of a gas chromatograph equipped with a flame ionization detector is directly proportional to the amount of sample introduced. Thus, a single calibration point is all that is required to permit the gas chromatograph to be used for the required analyses. This calibration point is provided by the independent analysis of the undiluted working gas mixture. In theory, this linear plot should pass through the origin since the absence of organic vapor should correspond with zero peak area. In practice, the best straight line fit through the data points approaches the origin closely but it may not intersect the origin in all cases.

All measurements were made with a gas chromatograph equipped with a flame ionization detector (FID). The analytical column was a 1/8-in diameter 6-ft long stainless steel tube packed with 10 percent OV-17 on Chromosorb W (AW-DMCS) 80-100 mesh. This column gave sharp peaks and short retention times for the six solvent vapors examined. The He flow was 80 ml/min, air flow 800 ml/min, H₂ flow adjusted to maximize the detector response for each vapor. The FID temperature was 210 °C and the column temperature was adjusted for each analysis.

The tank mixtures were diluted with air using a gas dilution system. A tube inserted loosely into the

⁴See, for example, Hughes, E.E. et al., "Gas Generation Systems for the Evaluation of Gas Detecting Devices," National Bureau of Standards Report No. NBSIR 73-292, October 1973.

output gas manifold was connected to a double-loop GC sampling valve with 5-ml loops, and thence to the house vacuum.

The double-loop valve permitted the sample in one loop to be flushed into the GC while the sample gas flowed through and conditioned the second loop, thereby permitting a more rapid sample introduction than could be attained with a single-loop GC valve.

The sample gas was drawn from the gas manifold at atmospheric pressure through a loop of the GC valve, at a rate of 600 ml/min as measured by a rotameter. Just before introducing a sample into the GC, the flow through the valve was stopped by shutting off the vacuum. A 10-sec wait allowed the sample to equilibrate at ambient atmospheric pressure. After the GC valve was turned to flush 5 ml of sample into the instrument, the vacuum was turned on to draw additional sample through the second loop. This stop-flow method was found to give better reproducibility of measurements than the procedure of sampling the gas while it flowed through the GC valve since it assured that all the samples were at the same (atmospheric) pressure.

Several determinations were made at each concentration, starting from the undiluted working standard at 5 x TLV or higher, down to zero concentration (air only). The results given in the next section show that the gas chromatograph response was linear with the gas concentrations as measured with the flowmeters of the gas dilution system, thereby demonstrating that the gas dilution flow controllers and meters were functioning in the expected manner.

5. EXPERIMENTAL RESULTS

5.1 Results of Gravimetric Analysis

Tables 5-10 present the results of the charcoal tube determinations of the vapor concentrations in the working standard gas tanks. The average gas concentrations rounded to the nearest 5-10 ppm are summarized in table 11.

The earliest 1973 determinations of chloroform, toluene and methylene chloride were not included in the final data averages because the early measuring techniques were relatively crude compared with the later measurements started in January 1974. Beginning at this time the individual flow rates were measured through each charcoal tube (instead of using an average flow calibration for the limiting flow orifice). The wet-test meter used to measure these flows was calibrated by two independent operators

Table 5. Charcoal tube gravimetry
chloroform

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
10/16/73	9.622	PP-C	1.626	1.0	1213	1207
	9.592	PP-C	1.626	1.0	1209	
	9.858	PP-D	1.680	1.0	1203	
	9.854	PP-D	1.680	1.0	1203	
10/29/73	17.310	PP-F	1.007	3.0	1176	1184
	17.390	PP-F	1.007	3.0	1181	
	17.580	PP-F	1.007	3.0	1194	
1/11/74	20.514	BC-C	1.7191	2.0	1222	1219
	21.239	BC-D	1.7881	2.0	1216	
4/29/74	21.255	BG-D	0.9051	4.0	1202	1205
	22.794	BG-E	0.9664	4.0	1208	
					Average: 1202	1204
					(S.D.=14)	

Chloroform Analysis:

Average of all 1974 measurements: 1212 ppm (S.D.=9)
Rounded value: 1210 ppm

Table 6. Charcoal tube gravimetry
toluene

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
11/1/73	6.965	PP-F	1.007	3.0	613	620
	7.110	PP-F	1.007	3.0	626	
1/21/74	8.400	BC-C	1.7346	2.0	643	648
	8.856	BC-D	1.7985	2.0	653	
1/22/74	8.471	BC-C	1.7463	2.0	644	650
	8.585	BC-C	1.7463	2.0	652	
	8.802	BC-D	1.8049	2.0	647	
	8.913	BC-D	1.8049	2.0	655	
5/1/74	14.031	BG-E	0.9715	6.0	639	645
	15.436	BG-F	1.0486	6.0	651	
					Average 642	641
					(S.D.=13)	

Toluene Analysis:

Average of 1974 measurements = 648 ppm (S.D.=6)
Rounded value: 650 ppm

Table 7. Charcoal tube gravimetry
methylene chloride

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
10/29/73	8.590	PP-F	1.007	0.5	4917	4917
	8.625	PP-F	1.007	0.5	4940	
	8.545	PP-F	1.007	0.5	4895	
1/23/74	15.302	BG-D	0.9116	1.0	4832	4849
	15.461	BG-D	0.9116	1.0	4883	
	16.365	BG-E	0.9693	1.0	4861	
	16.410	BG-E	0.9693	1.0	4874	
	17.844	BG-F	1.0554	1.0	4867	
	17.519	BG-F	1.0554	1.0	4779	
4/30/74	32.223	BG-E	0.9585	2.0	4839	4835
	34.973	BG-F	1.0422	2.0	4830	
Average:					4865	4867
(S.D.=45)						

Methylene Chloride Analysis:

Average of 1974 measurements: 4846 ppm (S.D.=33)
Rounded value: 4850 ppm

Table 8. Charcoal tube gravimetry
ethylene dichloride

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
3/12/74	3.860	BG-E	0.9696	1.0	984	978
	7.725	BG-E	0.9696	2.0	984	
	4.100	BG-F	1.0519	1.0	963	
	8.360	BG-F	1.0519	2.0	982	
3/13/74	15.520	BG-E	0.9667	4.03	983	984
	16.770	BG-F	1.0434	4.03	985	
4/30/74	10.608	BG-D	0.8974	3.0	974	975
	11.415	BG-E	0.9643	3.0	975	
Average:					979	979

Ethylene Dichloride Analysis:

Average of all 1974 measurements = 979 ppm (S.D.=8)
Rounded value: 980 ppm

Table 9. Charcoal tube gravimetry
1,1,1- trichloroethane

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
3/11/74	10.49	BG-E	0.9800	1.0	1962	
	10.49	BG-E	0.9800	1.0	1962	
	11.37	BG-F	1.0663	1.0	1954	
	11.45	BG-F	1.0663	1.0	1968	1961
5/1/74	20.326	BG-E	0.9719	1.99	1926	
	21.925	BG-F	1.0523	1.99	1919	1923
5/2/74	19.260	BG-D	0.9127	2.0	1934	
	10.270	BG-E	0.9726	1.0	1935	
	20.525	BG-E	0.9726	2.0	1934	
	10.998	BG-F	1.0528	1.0	1915	
	22.292	BG-F	1.0528	2.0	1940	1931
Avg. Concn.					1941	1938

1,1,1- Trichloroethane Analysis:

Average of all 1974 measurements: 1941 ppm (S.D.=18)
Rounded value: 1940 ppm

Table 10. Charcoal tube gravimetry
styrene - low concentration

<u>Date</u>	<u>Sample weight</u> (mg)	<u>Orifice</u>	<u>Flow rate</u> (l/min)	<u>Sampling time</u> (min)	<u>Gas concn.</u> (ppm)	<u>Average concn.</u> (ppm)
3/14/74	11.20	BC-C	1.7511	22.0	68.3	
	11.59	BC-D	1.7492	22.0	70.7	69.5
5/2/74	6.235	BG-D	0.9134	23.0	69.7	
	6.748	BG-E	0.9743	23.0	70.7	
	7.430	BG-F	1.0605	23.0	71.5	70.6
Average Concn.					70	70

Low-Styrene Analysis: 70 ppm (S.D.=1.2)

styrene - high concentration

7/22/74	9.339	BG-D	0.9116	5.0	481	
	9.806	BG-E	0.9718	5.0	474	
	10.541	BG-F	1.0605	5.0	467	474

High-Styrene Analysis: 474 ppm (S.D.=7)
Rounded value: 475 ppm

Table 11. Properties of compressed gas mixtures

Solvent ingredient	Molec. weight (g/mole)	TLV ^a / (ppm)	Max. concn. needed (ppm)	Saturation vapor pressure		Partial pressure inserted (mm)	Weight liquid injected (g)	Filled pressure (psia)	Calculated concn. (ppm)	(Rounded) avg. concn. measured (ppm)
				20 °C (mm)	25 °C (mm)					
Chloroform	119.38	50	125	150	190	65.4	—	1000	1265	1210
Toluene	92.13	200	500	21	27	27.0	—	875	597	650
Methylene chloride	84.93	500	2500	290	350	259.0	—	1000	5000	4850
Ethylene dichloride	98.96	50	250	65	80	44.3	—	837	1024	980
1,1,1-Trichloroethane	133.41	350	1750	100	120	79.8	—	786	1963	1940
Styrene (low concn.)	104.14	100	500	5	7	—	0.98	843	97	70
Styrene (high concn.)	104.14	100	500	5	7	—	1.025	150	562	475
							1.040	150	571	
							1.034	150	567	
(Mixed & Used Together)										
Carbon disulfide	76.14	20	100	290	350					
Vinyl chloride	62.50	0 ^{b/}	250	>760	>760					
Acetone	58.08	1000	5000	180	225					
Methyl ethyl ketone	72.11	200	1000	76	100					
Chlorobenzene	112.56	75	375	8.5	11.5					
Aniline	93.13	5	25	<1	<1					
Phenol	94.11	5	25	<1	<1					

a/ Federal Register 36, (157) Aug. 13, 1971 except vinyl chloride.

b/ The proposed TLV for vinyl chloride is zero ppm.

using entirely different methods. Special precautions were taken to eliminate static electricity effects during weighings, and temperature and humidity effects were minimized by adopting a standard operating procedure of permitting the charcoal tubes to equilibrate for 30-60 min before every weighing.

It is apparent that the vapor content of the compressed gas cylinders was relatively stable over the 2-6 months that measurements were made. The greatest apparent drop in concentration was a 1.5 percent decrease in trichloroethane concentration from 1961 to 1931 ppm. The standard deviation of the measurements (S.D. on tables 5-10) was about one percent of the concentrations.

5.2 Results of Gas Chromatographic Analysis

Tables 12 through 17 list the peak areas and retention times for chloroform, toluene, methylene chloride, ethylene dichloride, trichloroethane, and styrene together with the gas concentrations corresponding to the flow settings on the gas dilution system controls. Figure 5 is a plot of all the GC responses against the gas concentrations normalized as fractions of original concentrations of undiluted working standards. The linearity of the curves is a confirmation of the calibration of the flow controllers and meters on the gas dilution system instrumentation.

The standard deviation (SD) of each group of peak area measurements shown in tables 12-17 is about one percent with occasional excursions to 1.4 percent. The 12 ppm styrene mixture shows the widest variation in peak areas with a standard deviation of 1.8 percent.

6. SUMMARY AND CONCLUSIONS

A system has been developed for generation of test mixtures of organic solvent in air. This system consists of (1) working standards of compressed gases in cylinders, (2) a means of verifying the composition of these working standards at any time, (3) a demonstration that these standards may be diluted to any desired working concentration, which can be rapidly confirmed by gas chromatography.

An absolute method of gas analysis, charcoal tube gravimetry, showed the working standards to be stable over periods of 2 to 6 months; that is, gas mixtures measured over these periods showed no appreciable losses or decomposition. Should losses of vapor ever occur due to sorption on interior cylinder surfaces, the capability of the

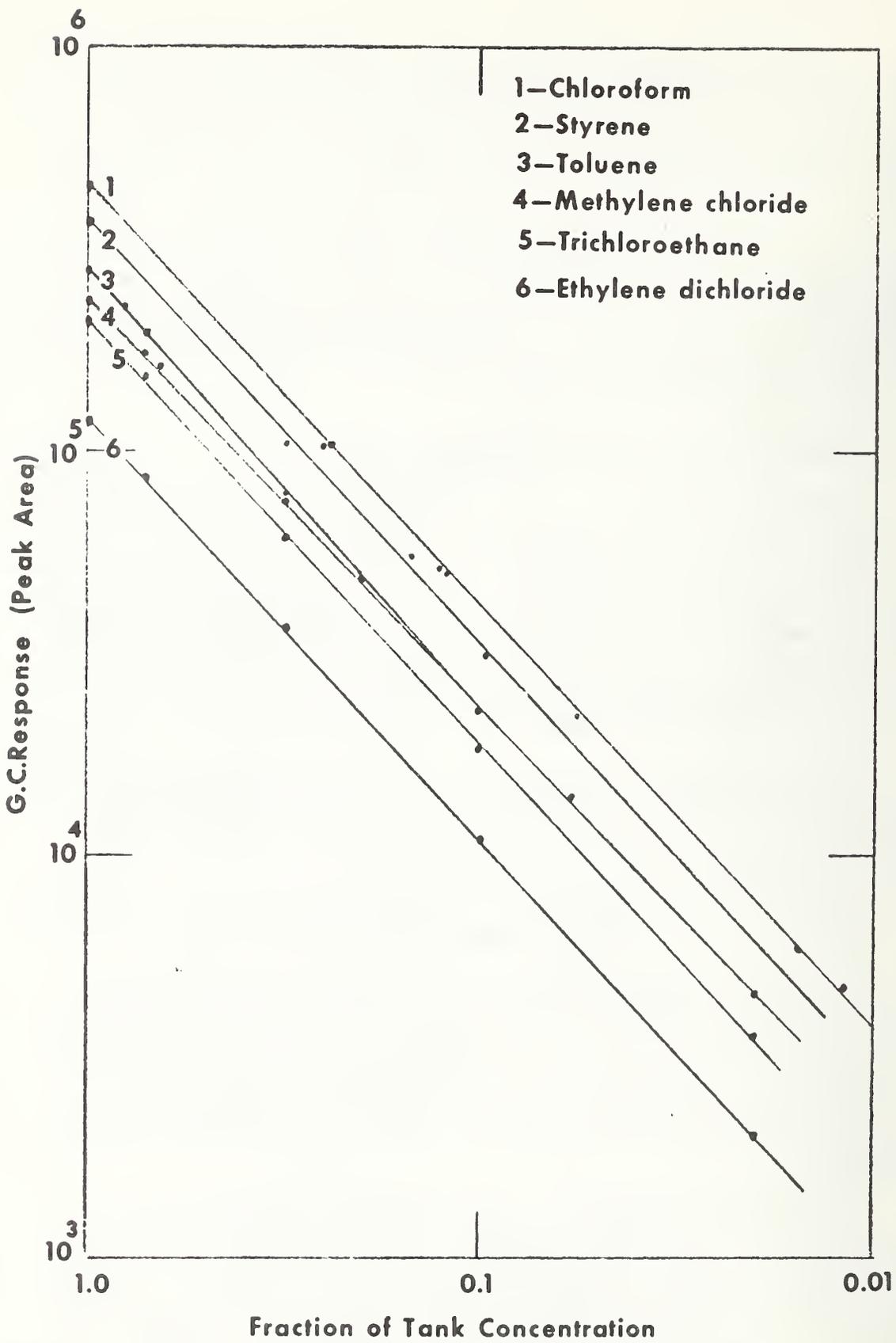


FIG. 5 G.C. RESPONSE VS. GAS CONCENTRATION

charcoal tube method to measure absolute vapor concentrations would permit these losses to be measured accurately, so that the integrity of the working standards would be maintained.

The standard deviation of all the charcoal tube measurements and the gas chromatographic analyses was one percent except for slight excursions of occasional data points to nearly 2 percent.

Table 12. Gas chromatographic analysis of vapor-air mixtures
chloroform (1210 ppm)

<u>Date</u>	<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
11/13/73	0.055	4.55	1.19	14.4	4739	4704	33
					4674		
					4698		
	0.055	3.59	1.51	18.3	5882	5810	63
					5825		
0.22	3.63	5.71	69.1	22030	22110	97	
				22230			
				22140			
				22030			
0.22	1.49	12.9	156	51000	51070	50	
				51100			
				51110			
				51080			
0.22	0.653	24.1	292	101600	102600	688	
				102700			
				103100			
				103000			
11/16/73	0.22	1.49	12.9	156	50150	50190	50
					50220		
0.22	0.653	25.2	305	103100	103500	500	
				103800			
11/27/73	0.57	0.22	72.2	874	327200	327500	235
					327600		
					327600		
2.12	0	100	1210	460800	461400	930	
				462500			
				461000			

Operating Conditions

Column Temperature 70 °C

Gases: He 60 psig, Air 42 psig, H₂ 11.2 psig

Peak retention times: Air 36 sec., chloroform 89 sec.

Table 13. Gas chromatographic analysis of vapor-air mixtures
toluene (650 ppm)

<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
0.219	3.48	5.92	38.5	13570 13560 14000 13640 13720	13700	181
0.219	2.029	9.74	63.3	23740 23920 23700 23980	23840	136
0.219	0.89	19.75	128	48090 48580 48340 49380	48600	450
0.219	0.489	30.9	201	77650 78900 78390 78960	78480	607
0.575	0.219	72.4	471	196100 198900 199000 199600	198400	1564
0.93	0.219	80.9	526	228900 229800	229400	640
2.135	0	100	650	282700 289700 284500 287800	286200	3160

Operating Conditions:

Column Temperature 100 °C

Gases: He 60 psig, Air 42 psig, H₂ 11.2 psig

Peak Retention Times: Air 19 sec., toluene 82 sec.

Table 14. Gas chromatographic analysis of vapor-air mixtures
methylene chloride (4850 ppm)

<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
0.041	2.029	1.98	96	4505 4574 4463 4576 4471 4546	4523	50
0.219	2.029	9.74	472	23100 23500 23300 23700 23340 23370	23390	202
0.219	0.489	30.9	1499	75710 78050 75690 77400 76160 77360	76730	1004
0.575	0.219	72.4	3511	174500 176800 174200 177400 175000	175600	1433
2.135	0	100	4850	241600 238400 244600 236700 242600 236200	240000	3417

Operating Conditions:

Column Temperature 80 °C

Gases: He 60 psig, Air 42 psig, H₂ 11.2 psig

Peak retention times: Air 20 sec., methylene chloride 41 sec.

Table 15. Gas chromatographic analysis of vapor-air mixtures ethylene dichloride (980 ppm)

<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
0.041	2.029	1.98	19.4	1977 1967 1989 1967 2011 1989	1983	17
0.219	2.029	9.74	95.5	10960 10780 11020 10820 10960 10820	10890	99
0.219	0.489	30.9	303	36890 36450 36970 36550	36720	254
0.575	0.219	72.4	710	86020 87120 85960 87950 85610 87290	86660	952
2.135	0	100	980	120500 118900 122000 118400 120900 119200	120000	1376

Operating Conditions:

Column Temperature 75 °C

Others: Same as table 14

Peak retention times: Air 18 sec., ethylene dichloride 83 sec.

Table 16. Gas chromatographic analysis of vapor-air mixtures
1,1,1-trichloroethane (1940 ppm)

<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
0.041	2.029	1.98	38	3612 3615 3563 3574 3523 3577	3577	34
0.219	2.029	9.74	189	18690 18410 18670 18540 18860	18630	169
0.219	0.489	30.9	599	64600 63270 65320 63900 64720 63020	64140	895
0.575	0.219	72.4	1405	158700 154200 156700 153900 157000	156100	1810
2.135	0	100	1940	214300 217000 214600 218400	216100	1966

Operating Conditions:

Column Temperature 90 °C

Others: Same as table 14

Peak retention times: Air 20 sec., trichloroethane 50 sec.

Table 17. Gas chromatographic analysis of vapor-air mixtures
styrene (475 ppm) ¹

<u>Flow of working standard (l/min)</u>	<u>Flow of diluent air (l/min)</u>	<u>Percent of working standard in mixture (percent)</u>	<u>Concn of solvent vapor in mixture (ppm)</u>	<u>G.C. peak area</u>	<u>Average of peak areas</u>	<u>S.D.</u>
0.055	2.029	2.6	12.4	3285 3301 3364 3331 3436	3343 ²	60
0.219	2.029	9.74	46.3	31440 31290 31790 31680	31550	227
0.219	0.489	30.9	147	105300 105900 106900 107300	106350	915
2.135	0	100	475	366900 367300 370400 369800	368600	1757
LOW STYRENE CYLINDER LK 152540:			70	55220 55070 55310 55370 55490	55290	158

Operating Conditions:

Column Temperature 125 °C

Gases: He 60 psig, Air 40 psig, H₂ 13.5 psig

Peak retention times: Air 20 sec., styrene 75-76 sec.

¹Three styrene cylinders connected together by a gas manifold.

²Low value, should be about 8,000 by comparison with other data points.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)			
<p>The development of gas generation systems is described. Stable mixtures of contaminant gases with air are stored in compressed gas cylinders at concentrations about five times the TLV. The cylinders are analyzed by charcoal tube gravimetry in which the weight increase of tared charcoal tubes is used to determine the organic component of the gas mixture. For use, the compressed gases are dynamically diluted with air to the needed concentrations in a gas-flow system.</p> <p>Data are presented to demonstrate (1) linearity of the gas dilution system as measured by gas chromatographic determinations of vapor concentrations; (2) precision of charcoal tube gravimetric measurements; and (3) stability of compressed gas mixtures of air with chloroform, toluene, methylene chloride, ethylene dichloride, 1,1,1-trichloroethane, and styrene at concentrations of 1210, 650, 4850, 980, 1940, and 475 ppm respectively.</p> <p>It is concluded that the methods of preparation and verification of these compressed vapor-air mixtures have general applicability. A wide variety of stable single-component vapor-air mixtures may be prepared and analyzed to one percent accuracy rapidly and routinely.</p>			
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Air sampling; chromatography; industrial hygiene; gas analysis; gas standards			
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